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Spatial variability in the coupling of organic carbon, nutrients, and phytoplankton pigments in surface waters and sediments of the Mississippi River plume

Laura A. Wysocki [a,*], Thomas S. Bianchi [a,1], Rodney T. Powell [b], Nina Reuss [c]

[a] Department of Earth and Environmental Sciences, Tulane University, New Orleans, LA 70118, USA
[b] Louisiana Universities Marine Consortium (LUMCON), Chauvin, LA 70344, USA
[c] Department of Geology, Lund University, Sölvegatan 12, SE-223 62 Lund, Sweden

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Abstract

River-dominated coastal areas are typically sites of active biogeochemical cycling, with productivity enhanced by terrestrial inputs of nutrients and organic matter. To examine the spatial variability and relationship between river discharge, phytoplankton, and organic carbon distributions, we analyzed surface water and sediment from the Louisiana shelf adjacent to the Mississippi River. Samples were collected during April and October 2000 to capture high and low river discharge, and were analyzed for dissolved and particulate organic carbon (DOC and POC), nutrients, and phytoplankton pigments. Pigments, determined by high performance liquid chromatography (HPLC), were also analyzed from sediment to evaluate marine carbon inputs to the seafloor. DOC in surface waters was generally within 200–300 μM, ranging up to 399 μM. Chlorophyll *a* ranged from below the limits of detection (BLD) up to 31 nM in surface waters, with higher values located further from the river mouth during high flow. Although community diversity increased during low discharge, diatoms dominated the phytoplankton population (50–80% of the community throughout the study) and consequently made more important contributions than other species to both the DOC and POC pools. Chlorophyll and degradation products (indicative of zooplankton grazing) observed in surface sediment indicated a transfer of autochthonous carbon from the highly productive photic zone to the sediment, coupling phytoplankton-derived POC in surface waters with organic carbon deposition in surface sediment. Cross-shelf changes in chlorophyll indicated a westward transport of phytoplankton that was directly and indirectly linked with river discharge and pigment decay dynamics.

Keywords: phytoplankton; pigment biomarkers; organic matter; benthic-pelagic coupling; Gulf of Mexico; Mississippi River plume

1. Introduction

High rates of primary production and organic matter remineralization along river-dominated coastal margins are largely the results of riverine inputs of terrestrially-derived dissolved and particulate materials (see review by Dagg et al., 2004, and references therein). For example, the Mississippi and Atchafalaya rivers deliver 60% of the nitrogen on the Louisiana shelf and provide the major pathway for the input of terrigenous organic materials to the Gulf of Mexico (Trefry et al., 1994; Turner and Rabalais, 1994; Bianchi et al., 2002). Lohrenz et al. (1997) observed a direct relationship between riverine nutrient fluxes and primary production in Louisiana continental shelf waters. Primary production across the Louisiana shelf is highly dynamic, with rates ranging from as low as 0.5 g C m^{-2} day^{-1} in winter months and up to 10 g C m^{-2} day^{-1} during the summer (Lohrenz et al., 1990, 1999; Redalje et al., 1994). According to a recent model by Dagg and Breed (2003), nitrogen availability in the

* Corresponding author.
E-mail address: lwysock@tulane.edu (L.A. Wysocki).
[1] Present address: Department of Oceanography, Texas A&M University, College Station, TX 77843-3146, USA.

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Mississippi River Plume (MRP) controls the structure of the phytoplankton community and interactions between different size classes of both phytoplankton and zooplankton. While there has been considerable work on the variability in productivity (Lohrenz et al., 1990; Redalje et al., 1994; Lohrenz et al., 1997, 1999) and phytoplankton composition (Bode and Dortch, 1996; Strom and Strom, 1996; Liu and Dagg, 2003; Dagg et al., 2004) within the MRP proper, little is known about the relationship between phytoplankton composition and nutrient variability across the Louisiana shelf, resulting from gradients of *in situ* "trophic" processing in the plume, as well as from external changes in river discharge.

While the Mississippi River is a major source of DOC to the Louisiana shelf, contributing an estimated 3.1×10^{-3} Pg DOC (Bianchi et al., 2004), contributions of DOC from *in situ* processes such as primary production, zooplankton grazing, and resuspension may also be significant, particularly during periods of high productivity (Benner and Opsahl, 2001). Substantial amounts of DOC can be produced *in situ* by phytoplankton exudation (Norrman et al., 1995; Fry et al., 1996) and bacterially-mediated decay of marine and terrestrially-derived POC (Biddanda and Benner, 1997). Temporal and spatial variability in DOC and particulate organic carbon (POC) derived from phytoplankton production is largely controlled by the same factors affecting variability in production itself, namely light and nutrient availability (Redalje et al., 1994; Lohrenz et al., 1999). However, this relationship is likely to be complicated by the highly dynamic character of the MRP, as well as riverine inputs of organic carbon. To our knowledge, no attempts have been made to examine DOC and POC variability with respect to phytoplankton composition on a finer spatial scale (e.g., beyond a few sampling transects) within the entire MRP region.

The vertical flux of terrestrial and marine-derived particles in plume regions is typically very high. In the case of the MRP, many of the large particulates that are in suspension rapidly sink once entering shelf waters (Trefry et al., 1994). Similarly, flocculation and adsorption processes occur with increasing ionic strength in Gulf waters, resulting in the aggregation of dissolved and colloidal materials into particulates (Scholkovitz, 1976; Sharp, 1983). In addition to these processes, the contribution of sedimenting phytodetritus to Louisiana shelf sediments also depends on seasonally variable vertical particulate fluxes and heterotrophic processing in the water column.

The overall goal of this study was to examine the relationship between river discharge and spatial changes in the abundance and composition of phytoplankton, organic carbon in surface waters, and sedimentary organic carbon (SOC) in surface sediments in the MRP region. Specifically, concentrations of DOC and nutrients in surface waters were compared with plant pigment concentrations and POC. We used plant pigment biomarkers in POC and surface sediments to examine the spatial variability in the sources of marine phytoplankton to SOC in the plume. While other studies have made measurements on phytoplankton production, nutrient uptake rates, and vertical particle flux rates, this is the first study to examine the relationship between bulk carbon, nutrients, and chemical biomarker measurements in the water column and surface sediments across an extensive spatial gradient under different river discharge periods in the MRP region.

2. Materials and methods

2.1. Site description and sampling

Mississippi River water flows west/southwest from the mouth of the river, depositing sediment along the southern Louisiana coast (Hitchcock et al., 1997). The general flow of this water results in a main depositional path between the 20 and 100 m isobaths (Corbett et al., in press). The area investigated in this study is the region incorporating and adjacent to the Mississippi River plume (Fig. 1), which we refer to hereafter as the Mississippi River Plume-influenced Region (MRPR).

Two cruises were conducted within the MRPR and receiving waters of the Louisiana shelf, which took place in April 5 to 12 and October 24 to November 1, 2000. The sampling times were chosen to represent high and low river flow, with discharges of $\sim$15,000 $m^3\ s^{-1}$ and 5000 $m^3\ s^{-1}$ in April and October, respectively.

Surface sediments (0–2 cm) and surface water samples (ca. 1 m depth) were collected on a grid of 50 sampling sites (indicated by the symbols on Figs. 2–5 and 7) that spanned the area of the plume and the surrounding waters. On both cruises, near surface water was continually monitored by the shipboard flow-through system, a PC-based Multiple Instrument Data Acquisition System (MIDAS), collecting salinity, temperature, and fluorescence data using a Sea-bird Electronics SBE 21 Thermosalinograph; a Sea-Bird Electronics SBE 38 Remote Digital Immersion Thermometer; and two Turner Designs Model 10 Series Fluorometers. Water column samples were collected in opaque containers from a rosette of Niskin bottles and immediately filtered through GF/F filters (nominal pore size = 0.7 μm). Filters for pigment analyses were kept in the dark, stored in liquid nitrogen on-board ship and stored in a −80 °C freezer in the laboratory, prior to pigment analysis. Sediments were collected using a Benoit box-core; the upper 2 cm were collected and stored frozen for later analyses. Sediment was homogenized, sub-sampled, freeze-dried, and ground for biomarker analyses (Bianchi et al., 1995).

2.2. POC, DOC and particulate nitrogen analyses

Frozen sediment samples were freeze-dried with a LABCONCO (Freezone-6) System. Filters were dried in an oven at 50 °C until the dry weight stabilized. A small amount of sediment or one filter was placed in a combusted glass vial and acidified with 12 N HCl vapor for over 24 h (Hedges and Stern, 1984), then dried at 40 °C for 20–24 h. Carbon (C) and nitrogen (N) analyses were conducted on an elemental analyzer (EA1108, FISONS Instruments) at the Tulane Coordinated Instrument Facility (CIF).

Water samples were filtered through combusted 47 mm GF/F filters using a peristaltic pump. Filtrate was collected